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Modelling of Palladium Gold alloy- dielectric stratified loaded plasmonic waveguide for hydrogen detection at room temperature

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Abstract. A plasmonic waveguide loaded with metal - dielectric stratified layer is reported for room temperature hydrogen sensing. Pd-Au alloy with atomic ratio 3:1 (Pd/Au) is used as the metal and air is used as dielectric layer in the sensor. When hydrogen is loaded in the waveguide the alloy absorbs hydrogen and the effective permittivity of the stratified medium changes. Density functional theory and Bruggeman's effective medium theory are used to calculate the permittivity of bare and hydrogenated alloy. At a specific wavelength the change in the absorption loss of the device on hydrogen absorption is used as the measurement for hydrogen detection. At 633 nm the loss decreases almost linearly with increasing hydrogen concentration. For a device length of 10 μm the change of loss is achieved about 0.03 dB for 1 % change of hydrogen concentration.

1. Introduction

Hydrogen is highly flammable gas and can burn at very low concentration of about 4% in the air. Safe and easy detection of very low concentration of hydrogen gas is a fascinating area of study. Pd is an important material for hydrogen sensing application [1-5]. But there are certain limitations of using Pd. During hydrogen absorption desorption cycle Pd membrane suffers from embrittlement and crack due to α to β phase transformation as β phase contributes more lattice expansion compared to α phase [1,2]. Alloying Pd with other metals like Au, Ag reduces volume expansion thereby reducing the probability of crack formation hence producing more stable structure. The rate of hydrogen permeation in Pd-Au and Pd-Ag alloy is higher than that of pure Pd [6, 7]. Two times higher hydrogen permeability than pure Pd is achieved using $Pd_{0.8}Au_{0.2}$ alloy [8]. Pd-Au alloy is also more resistant to sulfur poisoning w.r.t. other alloys [9]. Additionally inclusion of Au in Pd can overcome some limitations of Pd as plasmonic material.

Surface plasmon resonance based hydrogen sensor is growing area of research due to safe, hazardless, fast detection and high sensitivity. In this work we have designed stratified metal dielectric composite loaded four layer plasmonic waveguide for room temperature hydrogen sensing. Pd-Au alloy with atomic concentrations of 75% and 25% for Pd and Au is used as metal layer in the stratified media. To calculate the response of designed waveguide the permittivity of the alloy should be evaluated. Density Functional Theory (DFT) is a useful method to solve Schrödinger equation for many electron systems and can be used to evaluate various properties of any material. So we here employ DFT to calculate the complex permittivity of bare and hydrogen loaded alloy. We have used metal dielectric stratified layer instead of single metal layer to compensate the huge loss of the waveguide caused by metal. When Pd_3Au alloy absorbs hydrogen the permittivity of the alloy gets changed accordingly the loss of the waveguide for a specific wavelength changes. At wavelength 633 nm we have calculated the absorption loss that decreases almost linearly with increasing hydrogen

concentration. For a device length of 10μm the decrease of absorption loss is 0.03db for 1 % change of hydrogen concentration.

2. Theoretical calculations

Plane wave Density Functional Theory (DFT) [10, 11] is used to calculate dielectric function of bare and hydrogen loaded Pd_3Au alloy. Vienna Ab Initio Simulation Package (VASP) [14] using projector-augmented wave (PAW) method [17] is used to carry out DFT calculation. Electron exchange correlation effects are described using GGA (generalized gradient approximation) with PBE (Perdew, Burke and Ernzerhof) functional [15, 16]. Permittivity is calculated by evaluating direct electronic transitions from occupied to higher energy unoccupied electronic states.

For metallic system the complex permittivity (ε(ω)) consists of interband and intraband terms. Imaginary interband part is calculated from band diagram by taking real transitions from valence band to conduction band as shown in Equation 1 [18].

$$\mathrm{Im}\left[\varepsilon_{\alpha,\beta}^{inter}(\omega)\right]=\frac{4\pi^2e^2}{V}\lim_{q\to 0}\frac{1}{q^2}\sum_{a,b}2f_{bK}\left\langle u_{aK+e_\alpha q}\middle|u_{bK}\right\rangle\left\langle u_{bK}\middle|u_{aK+e_\beta q}\right\rangle\times \left[\delta\left(\xi_{aK}-\xi_{bK}-\omega\right)-\delta\left(\xi_{aK}-\xi_{bK}+\omega\right)\right] \quad (1)$$

Here, α, β represent different Cartesian directions, δ function generate peaks at transition energies $\omega=\xi_{aK}-\xi_{bK}$ where a and b refer to two different energy bands, q is the wave vector for a given K point in first Brillouin zone, transition probability is given by $\left\langle u_{aK+e_\alpha q}\middle|u_{bK}\right\rangle\left\langle u_{bK}\middle|u_{aK+e_\beta q}\right\rangle$ where u represents the component of Bloch wave function having periodicity of lattice and V is the volume of unit cell.

Real part of the dielectric function is calculated from imaginary part using Kramers-Kronig transform as given in Equation 2.

$$\mathrm{Re}\left(\varepsilon^{inter}(\omega)\right)=\frac{1}{\pi}\rho\int_{-\infty}^{+\infty}\frac{\mathrm{Im}\left[\varepsilon^{inter}(\omega')\right]}{\omega'-\omega}d\omega' \quad (2)$$

The intraband contribution to the optical properties affects mainly the low energy infrared part of the spectra. It can be described via Drude term given in Equation 3,

$$\varepsilon^{intra}(\omega)=1-\frac{\omega_p^2}{\omega^2+i\gamma_d\omega} \quad (3)$$

Where, ω_P is plasma frequency and γ_d is the damping parameter.

ω_P represents the intraband free electron plasma frequency tensor as given in Equation 4,

$$\omega_p^2(\alpha,\beta)=-\frac{4\pi e^2}{V}\sum_{b,K}2\frac{\partial f(\xi_b)}{\partial\xi_b}\left(\hat{e}_\alpha\frac{\partial\xi_b(K)}{\partial K}\right)\times\left(\hat{e}_\beta\frac{\partial\xi_b(K)}{\partial K}\right) \quad (4)$$

Fully occupied bands do not contribute to the plasma frequency.

Damping factor γ_d is calculated from plasma frequency ω_p and conductivity σ using Equation 5 [20].

$$\gamma_d=\frac{\omega_p{}^2\varepsilon_0}{\sigma} \quad (5)$$

This intraband contribution is summed up with interband part to get the total dielectric function of the bare and hydrogenated alloy.

The Monkhorst-Pack mesh with 8x8x8 K grid is used for the energy calculation. Plane wave energy cut off is set to 400 eV to ensure the convergence of the total energy. For optical dielectric

function calculations 16x16x16 K point grid is chosen. Geometric relaxations are done using conjugate gradient (CG) algorithm until the forces on the atoms are lower than 0.02 eV/Å. For the integration of the Brillouin zone the first order Methfessel-Paxton method with a value of 0.2 eV is used.

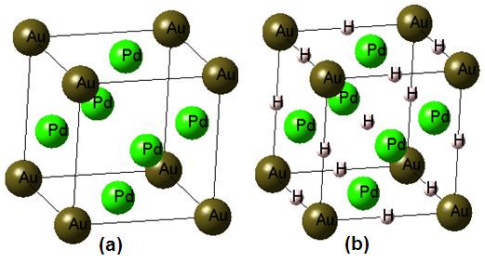

Figure 1 Atomic configurations of (a) Pd_3Au (b) Pd_3AuH_4.

For DFT calculation of Pd_3Au alloy we have used $L1_2$ structure in which Au atoms occupy corner positions whereas Pd atoms are placed in face positions [Fig. 1a]. This crystal structure is reported the most stable structure for Pd_3Au [12, 13]. For hydrogen loaded alloy hydrogen atoms are placed in octahedral interstitial sites of the Pd_3Au lattice shown in Fig. 1b. Here we consider inhomogenous distribution of hydrogen atoms in the alloy film in which both pure crystalline Pd-Au (α) phase and hydrogenated Pd-Au-H (β) phase are present together. Bruggeman's effective medium approximation [19] is used to calculate the effective dielectric function of the hydrogenated alloy having both the phases [Equation 6]. For α and β phases dielectric functions of pure Pd_3Au [Fig. 1a] and Pd_3AuH_4 [Fig. 1b] are considered.

$$f_\beta \cdot \frac{\varepsilon_\beta - \varepsilon_{eff}}{\varepsilon_\beta + 2\varepsilon_{eff}} + (1 - f_\beta)\frac{\varepsilon_\alpha - \varepsilon_{eff}}{\varepsilon_\alpha + 2\varepsilon_{eff}} = 0 \qquad (6)$$

Where ε_α, ε_β are dielectric functions of α and β phases respectively, f_β is the fraction of β phase.

For room temperature hydrogen sensing we have designed a 4 layered plasmonic waveguide shown in Figure 2b. The waveguide consists of silica substrate, higher index silica-titania film act as guiding layer, metal dielectric stratified layer on top of the guiding layer, air as the cover region. The stratified medium consists of periodic layers of Pd_3Au alloy film and air [Figure 2a]. From effective medium theory the permittivity of the stratified medium is calculated using equation 7.

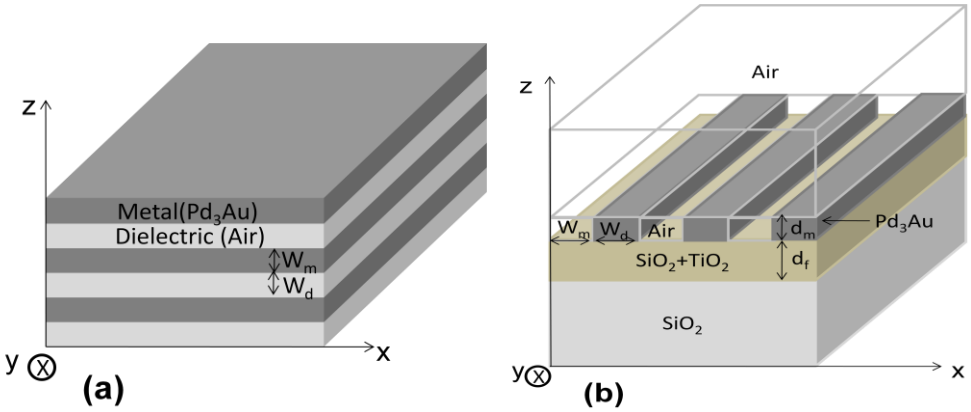

Figure 2. Schematic of (a) stratified medium (b) four layer waveguide loaded with the stratified layer. The waveguide parameters are optimized to achieve higher sensitivity. The values of the parameters are w_m=50nm, w_d= 8nm, d_f=580nm, d_m=15 nm. The refractive index of substrate (SiO_2) is 1.4573 and that of guided layer (SiO_2+TiO_2) is 1.7264.

$$\varepsilon_x = \varepsilon_y = \frac{w_m\varepsilon_m + w_d\varepsilon_d}{w_m + w_d} \qquad \text{And} \qquad \varepsilon_z = \frac{w_m + w_d}{\frac{w_m}{\varepsilon_d} + \frac{w_d}{\varepsilon_m}} \qquad (7)$$

Where w_m, w_d are thicknesses and ε_m and ε_d are permittivities of the alloy layer and air respectively. ε_x, ε_y are designated as parallel orientation permittivity and ε_z as perpendicular orientation permittivity.

The plot of ε_x and ε_z are shown in Figure 3. As ε_x has negative real part in a wide wavelength region we choose parallel orientation for the metal dielectric stratified layer. The response of the waveguide is studied analytically.

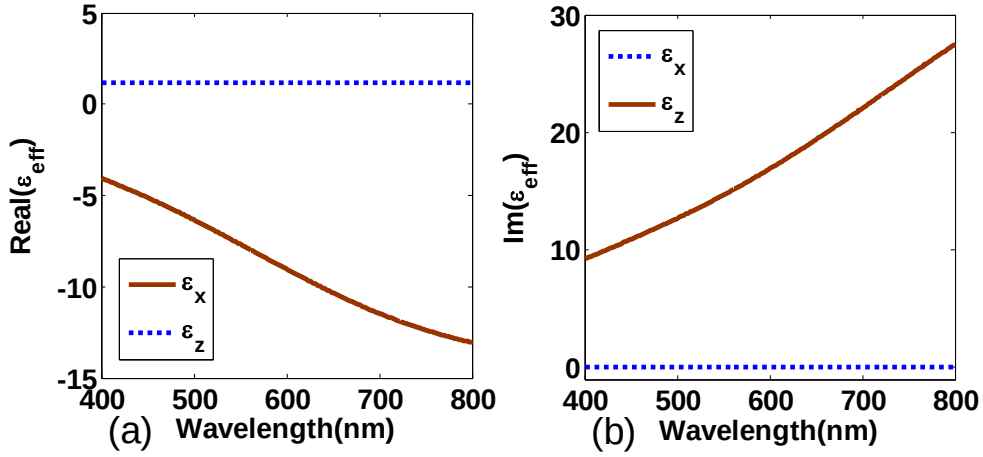

Figure 3. (a) Real part and (b) Imaginary part of effective permittivity of stratified medium for parallel (ε_x) and perpendicular (ε_z) orientation.

3. Results & Discussions

When the waveguide comes in contact with hydrogen gas the alloy absorbs hydrogen accordingly the permittivity of the alloy changes. As described in section 2 Bruggeman's effective medium theory is used to calculate permittivity of hydrogen loaded alloy. In Figure 4 we have plotted the variation of permittivity of the stratified layer on hydrogen absorption. It shows that with increasing hydrogen concentration both the real and imaginary part of complex permittivity decrease.

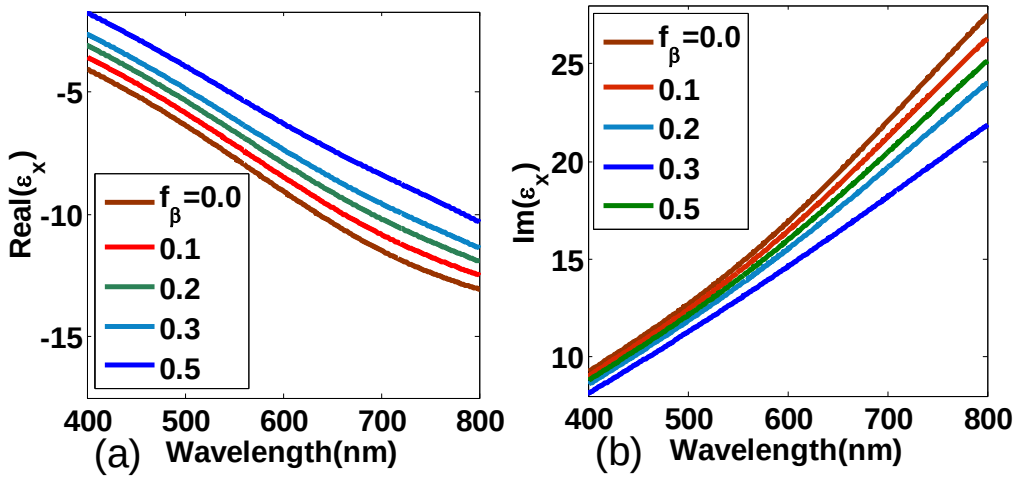

Figure 4. (a) Real part and (b) Imaginary part of permittivity of the stratified medium for different hydrogen concentration. Here f_β denotes the fraction of hydrogenated β phase to pure crystalline α phase of the alloy. With increasing hydrogen concentration f_β will increase.

We have analytically calculated the effective index of fundamental TM mode of the waveguide [21]. The mode field for fundamental TM mode at 633 nm is shown in Figure 5. The change of absorption loss of the waveguide at 633 nm on hydrogen loading is calculated. The waveguide parameters are optimized to achieve high value of sensitivity.

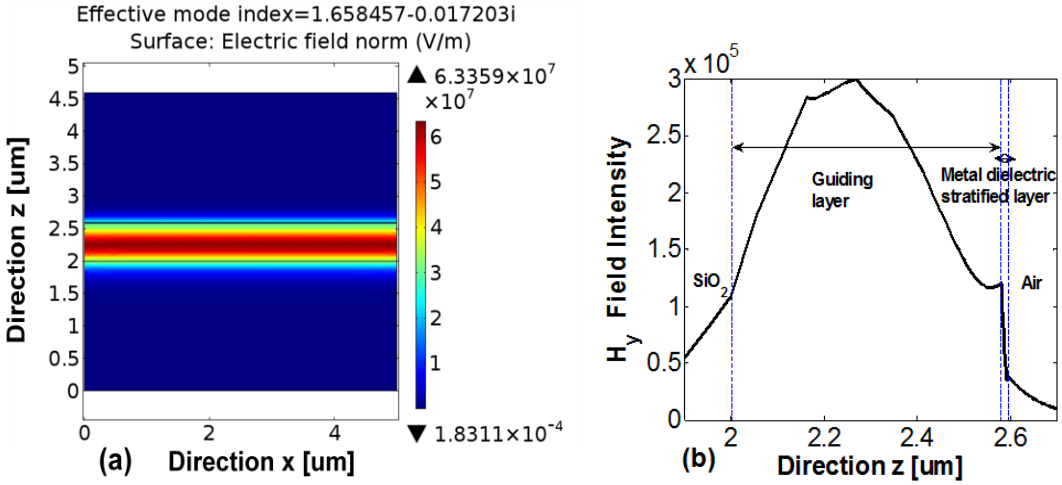

Figure 5. (a) Mode field of fundamental TM mode at 633 nm of the 4 layer stratified metal dielectric composite loaded plasmonic waveguide, (b) Intensity profile of normal component of magnetic field (H_y). The waveguide parameters are given in Figure 2.

The plot of absorption loss with variation of hydrogenated phase [Figure 6] shows the loss decreases almost linearly with increasing hydrogen concentration. The use of stratified layer instead of pure metal layer compensates the loss incurred by metal. In case of using single metal layer the absorption loss is too high to detect the transmitted power at output of the device. The slop of the graph is 0.3dB/0.1 fractional change of f_β.

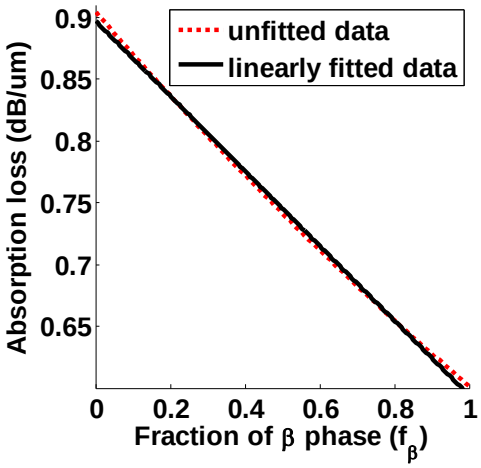

Figure 6. Plot of absorption loss of the waveguide with fraction of β phase to α phase for fundamental TM mode at 633 nm.

4. Conclusions

In this work we have reported four layer plasmonic waveguide consists of metal dielectric stratified layer for detection of hydrogen gas at room temperature. Pd_3Au alloy is used as metal layer due to its

ability of absorbing hydrogen. The optical permittivity of the alloy is calculated using DFT. Bruggeman's effective medium theory is used to calculate the effective permittivity of hydrogenated alloy considering inhomogenous distribution of hydrogen atoms. During hydrogen absorption in the alloy the effective index of stratified medium changes and the overall response of the waveguide varies accordingly. The absorption loss of the waveguide for fundamental TM mode is calculated analytically. The loss at 633 nm decreases almost linearly with increasing hydrogen concentration. For 1% change of hydrogen concentration the loss will change about 0.03 dB for a device length of 10μm. The use of stratified layer instead of pure metal layer reduces the huge loss of metal so that output power can be detected properly.

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